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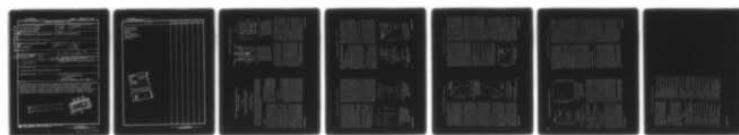
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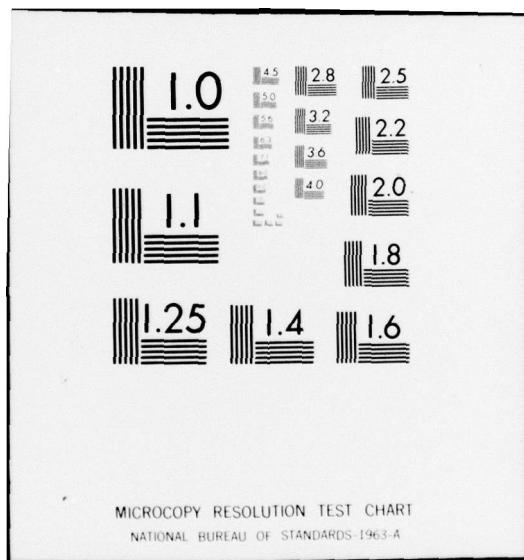
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The high temperature thermochemistry of inorganic materials naturally falls into three principal but related areas of research: Heat of Mixing Calorimetry, Solution Calorimetry, and Reaction Calorimetry of Solids. A brief survey will be presented of the development of modern high temperature reaction calorimetry, and of its application in these areas. Emphasis will be placed on the author's work on oxide melt solution calorimetry and on reaction calorimetry of solids.

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3. High Temperature Thermochemistry of Inorganic Materials

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(Invited lecture presented to
the 11th Japanese Calorimetry Conference)

The high temperature thermochemistry of inorganic materials naturally falls into three principal but related areas of research: Heat of Mixing Calorimetry, Solution Calorimetry, and Reaction Calorimetry of Solids. A brief survey will be presented of the development of modern high temperature reaction calorimetry, and of its application in these areas. Emphasis will be placed on the author's work on oxide melt solution calorimetry and on reaction calorimetry of solids.

1. Introduction

The applications of high temperature reaction calorimetry to problems of inorganic materials naturally fall into 3 categories: Heat of Mixing Calorimetry, Solution Calorimetry, and Reaction Calorimetry of Solids. Although these applications often can be carried out in the same type of calorimeter, to some extent they represent three different but related scientific traditions.

2. Calorimeter Design

Historically, two different principles of design have been adopted in high temperature reaction calorimetry. In one approach one has attempted to extend to high temperatures the **adiabatic** or **nearly adiabatic** designs which have proved so successful in room temperature and low temperature calorimetry. Among many others the adiabatic reaction calorimeter of Kawakami¹⁾ on liquid alloys carried out at Tohoku University nearly 50 years ago. Our own thermochemical studies of liquid metals²⁾ and of fused salts³⁾ represent direct extensions of the type of research initiated by Kawakami.

The first example of high temperature **solution calorimetry** is the work of Ticknor and Bever⁴⁾, who in 1952 pioneered the technique of **tin solution calorimetry**. This method has contributed greatly to the development of the thermochemistry of solid alloy systems during the past 25 years. Our own work on **oxide melt solution calorimetry**, developed in collaboration with Yokokawa in 1964⁵⁾, extended high temperature solution derived from the early adiabatic design of Kub-

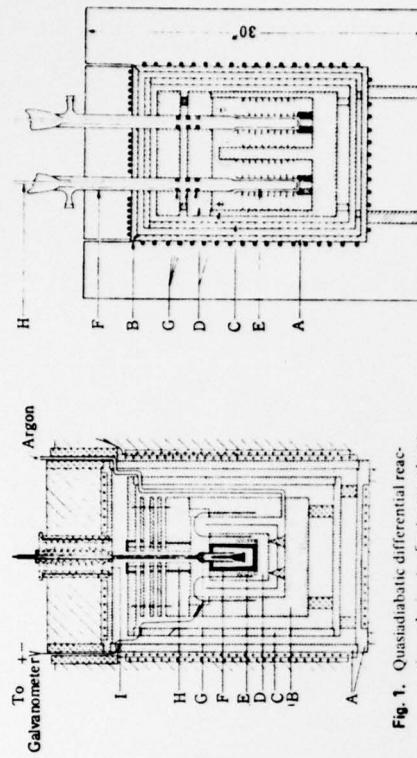


Fig. 1. Quasiadiabatic differential reaction calorimeter for temperatures below 500°C. A, furnace core with main heaters; B, constant temperature jacket (aluminum); C, heavy shield (steel); D, calorimeter block (aluminum); E, calibration heater; F, removable crucible (graphite); G, charging or stirring device (graphite); H, inner plug; I, outer plug.

scheski and Walter, we did not aim at adiabatic operation, but tried, as far as was convenient, to reduce the heat leak. An important feature of this apparatus was that temperature was measured differentially between the calorimeter and the surrounding jacket.

This calorimeter proved quite successful in studies of the heats of mixing of liquid metals²⁾ and for tin solution calorimetry below 500°C¹⁰⁾. However, when we attempted to use this design at temperatures up to 700–800°C, we found that the heat leak became intolerably large. Thus, the quasiadiabatic design, which had proved very useful below 500°C, seemed to have little to offer above this temperature. We concluded that precision reaction calorimetry above 500–600°C would require a new and different approach.

This new and different approach was provided by the integrated heat flux design of Tian and

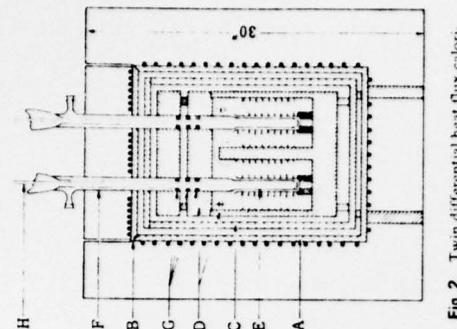


Fig. 2. Twin differential heat flux calorimeter for temperatures below 500°C. A, main heater; B, top heater; C, heavy shield (steel); D, aluminum jacket; E, calorimeter; F, protection tube (stainless steel); G, radiation shields; H, manipulator tube; I, O—O thermopile.

Calvet, the monograph of Calvet and Pratt¹¹⁾, which appeared in 1956, offered solutions to some of our problems. Calvet's work induced us to develop our first twin microcalorimeter for high temperature work, based on a modified Tian-Calvet design³⁾. The apparatus, which is shown in Fig. 2, was built in 1958–59 and is still in operation. However, the original chromel-alumel thermopile has been replaced by a Pt-Pt13Rh plate.

The following aspects of the Calvet type design are of particular significance:

(1) The temperature sensitive element consists of a multiple junction thermopile which measures the temperature difference between the external surface of the calorimeter proper and the internal surface of the surrounding jacket. By varying the number of thermocouples, the sensitivity of the apparatus can be varied within very wide limits.

(2) By changing the diameter (and the mass) of the

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calorimeter its time constant can be adjusted. We have found a diameter of about 25 mm to be convenient for many high temperature applications.

(3) Since the Calvet type apparatus is an integrated heat flux device, it is not a high precision instrument. In this respect it is certainly inferior to the adiabatic design below 500°C. On the other hand, it is a very simple, convenient and reliable calorimeter, and we have achieved very nearly the same precision at 1000°C as near room temperature.

(4) The twin construction is particularly useful at high temperature since it, to some extent, eliminates the need for elaborate and costly temperature control.

(5) If very good temperature control is available, it is sometimes possible to dispense with the twin construction and to still obtain very satisfactory calorimeter performance. This is true, in particular, for short term experiments such as, for example, many heat of mixing experiments.

We show in Fig. 3 a schematic diagram of a

single unit Calvet type calorimeter which has proved quite satisfactory at temperatures up to about 1000–1100°C. Since this apparatus has cylindrical symmetry, it is obviously simpler and cheaper in construction than the corresponding twin calorimeter. The instrument shown in Fig. 3 was built from sintered alumina components and should, in fact, be satisfactory for many applications even above 1100°C. However, where high baseline stability is important, it generally is desirable to retain the twin construction. A twin apparatus built from sintered alumina components and designed for operation above 1100°C is shown in Fig. 4.

At this time there have been a very large number of different applications of high temperature reaction calorimetry in various areas of inorganic chemistry; limitations of space and time will prevent me from discussing most of these applications in detail. Thus, I shall have nothing more to say here about the thermochemistry of liquid alloys, about mixtures of simple fused salts, and about tin solution calorimetry. However, I shall give a somewhat more detailed discussion of the principles and

applications of oxide melt solution calorimetry, and also say something about high temperature reaction calorimetry of solids.

3. Oxide Melt Solution Calorimetry

We give in Fig. 5 a schematic diagram of the experimental arrangements which have proved useful in oxide melt solution calorimetry. In our early work with Yokokawa we explored the potential of liquid vanadium pentoxide (V_2O_5) as a calorimetric solvent near 700°C (12). The results of this early exploration are summarized in Fig. 6, which gives the enthalpy changes associated with the solution of simple oxides, MO , in V_2O_5 . Note in particular that for the oxides of the alkaline earth metals the enthalpies of solution change systematically in the sequence

$BeO > MgO > CaO > SrO > BaO$

with small positive values for BeO and quite large negative values for BaO. This is, of course, the order of increasing ionic radius of the cation and of increasing basicity of the solute oxide, which is consistent with the fact that the solvent V_2O_5 is a very strongly acidic oxide. These early results

immediately suggest that an understanding of the elements of acid-base chemistry of melts is essential in any meaningful discussion of possible solvents for oxide melt solution calorimetry.

It is convenient to discuss the acid-base character of oxides and oxyd melts in terms of the Lux-Flood^{13,14} approach, which is analogous to the well-known Brønsted-Lowry scheme for protonic acids. According to Lux and Flood a suitable measure of the basicity of the melt is the oxygen ion activity, which is determined by the equilibrium:



The stronger the base, the higher the oxygen ion activity.

For the vanadium (V)-oxygen system we may write a series of possible (but not necessarily realized) consecutive acid-base steps, which involve species such as V^{4+} , VO^{3+} , VO_2^{+} , V_2O_5 , $V_2O_4^{2-}$, and VO_3^{2-} . Similarly we may for each oxide MO consider the species M^{2+} , MO , MO_2^{2-} , etc. When a basic solute MO is added to liquid V_2O_5 , this will give rise to the formation of vanadate species such as VO_3^{2-} , $V_2O_4^{2-}$, and VO_2^{+} (or

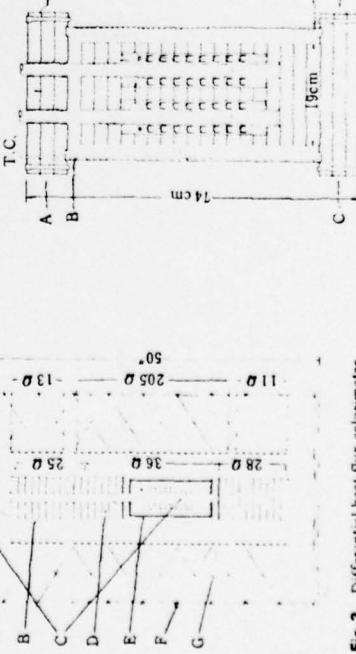


Fig. 3. Differential heat flux calorimeter for high temperatures (alumina)
A, main heater (Kanthal); B, inside heater (Pt-40Rh); C, protection tube; D, alumina disks; E, calorimeter jacket (alumina); F, water cooling; G, insulation; ⊙ – thermopile.

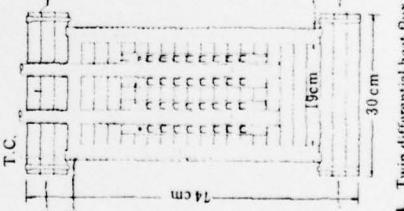


Fig. 4. Twin differential heat flux calorimeter for high temperatures (alumina)
A, main heater (Kanthal); B, inside heater (Pt-40Rh); C, protection tube; D, alumina disks; E, calorimeter jacket (alumina); F, water cooling; G, insulation; ⊙ – thermopile.

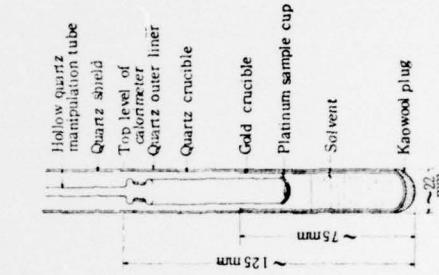


Fig. 5. Schematic diagram of calorimetric arrangements used in oxide melt solution calorimetry.

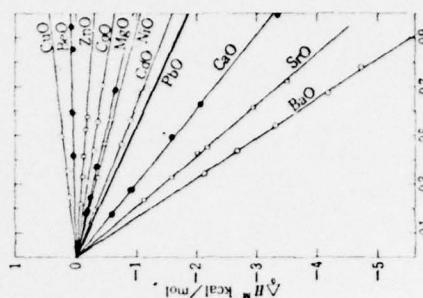


Fig. 6. Molar integral enthalpies of mixing of liquid V_2O_5 plus solid oxides at 700°C.

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polymeric forms of these). To a first approximation the magnitude and sign of the enthalpy change associated with the solution process

$$\text{MO}_3 + \text{V}_2\text{O}_5(l) = \text{M}^{2+} + \text{Vanadate (in V}_2\text{O}_5)$$

may be considered a measure of the tendency of this acid-base reaction to proceed from left to right, i.e., of the relative strength of V_2O_5 and M^{2+} as acids or of MO and vanadate as bases. The stronger the base MO (or the weaker the corresponding acid M^{2+}) the more negative the partial enthalpy of solution (ΔH_{sol}).

If the solute oxide M_nO_m is very acidic, e.g., has an acidity which approaches that of the solvent V_2O_5 , the acid-base character of the dissolution process in large measure will be suppressed. Under these conditions the enthalpy of solution no longer will serve as a meaningful measure of the relative acid-base strengths of the solutes. For this purpose one should, of course, instead use an oxidic solvent of basic character, such as, e.g., liquid PbO.

The vanadate- V_2O_5 mixtures which result from the dissolution of basic oxides in V_2O_5 are examples of buffered acid-base melts. Since most mixed oxide compounds contain two or more components of different acidity, it usually will be most convenient to use buffered melts as calorimetric solvent. This also has the practical advantage that in the buffered regions the enthalpies of solution of acidic or basic oxides tend to vary less with composition.

In 1967 Holm and Kleppa¹⁵ published the results of a calorimetric investigation of the PbO- B_2O_3 system carried out at 800°C. In this work the partial enthalpies of solution (actually $\Delta f/\Delta n$ of $\text{PbO}(s)$ and $\text{B}_2\text{O}_3(l)$) were measured at compositions between about 1/7 mole per cent and about 67 mole per cent B_2O_3 . At higher B_2O_3 contents the melts were too viscous to allow precise calorimetry by the direct mixing approach.

The results are shown in Figs. 7 and 8. Since the partial enthalpies of both components were measured, it was possible to check the internal consistency of the results by means of the Gibbs-Duhem equation. The results of this check are indicated as broken lines in the figures. On the whole there is reasonable agreement between the

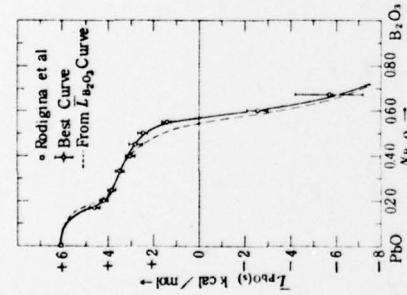


Fig. 7. $\Delta H_f \Delta n$ for solid $\text{PbO-B}_2\text{O}_3$ melts at 800°C. Enthalpy of fusion of PbO from E. N. Rodina, K. Z. Gomel'skii, and V. F. Luginina, Russ. J. Phys. Chem. **35**, 884 (1961).

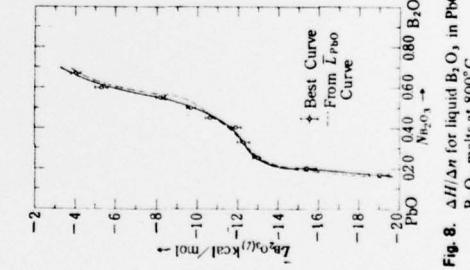


Fig. 8. $\Delta H_f \Delta n$ for liquid B_2O_3 in $\text{PbO-B}_2\text{O}_3$ melts at 800°C.
Calculated and measured data.
The data suggest interesting changes in the

acidity of the melt as the composition varies from basic in the high PbO region to acidic in the high B_2O_3 range. We interpreted the results to indicate that the liquid lead borate system contains at least two complex borate anions, which have oxygen-boron ratios of about 3.5/4.0 and 1.84/1.91, respectively. These ratios were obtained by attempting to locate the two steeply rising parts of the partial enthalpy versus composition curve. Between these two compositions the curves are flatter, which presumably reflects the presence of both of the two borate anions in comparable amounts, i.e., a buffer region. Most of our early calorimetric work was based on the use of melts with a $\text{MO}_3\text{B}_2\text{O}_5$ ratio of 3:1. However, as a result of the work by Holm and Kleppa we now prefer a somewhat more acid melt with a ratio of 2:1.

The principal applications of oxide melt solution calorimetry may be considered to fall into the following broad categories:

- (1) Determination of enthalpies of formation of refractory mixed oxides (e.g., the spinel family^{16,17}).
- (2) Enthalpies of phase transformations (e.g., Al_2SiO_5 ^{18,19}, TiO_2 ²⁰, SiO_2 ²¹).
- (3) Cation disorder in mixed oxides (e.g., spinels²², feldspar²³, sillimanite²⁴).
- (4) Mineralogical reaction and equilibria (e.g., jadeite²⁵, cordierite-sapphirine²⁶).

We show in Fig. 9 the results of our determination of the enthalpies of formation (from the pure oxides) for a series of 2-3 types aluminate, ferrite, spinel, and silicate minerals.

In their work Fig. 10, which shows the dependence of the configurational entropy on the parameter x in view of this graph it will readily be understood why some spinels with significant positive enthalpies of formation may well be stable at elevated temperatures.

High temperature cation disorder is a general problem in mixed oxide phases at high temperature. Another important example is provided by the feldspar family, such as, for example, in the sodium feldspar $\text{NaAlSi}_3\text{O}_8$ (albite).

In the albite structure the Al and Si atoms occupy 4 distinctly different crystallographic sites, each of which is surrounded by four oxygen atoms in tetrahedral coordination. If we designate these

manganese-, and gallate spinels involving the same divalent cations (Navrotsky and Kleppa¹⁶). Note in particular the near zero enthalpies of formation of the nickel spinels, and the positive values for all the copper spinels. More recent work by Muller and Kleppa¹⁷ shows that copper chromite similarly has a positive enthalpy of formation. The positive enthalpies indicate that these compounds must be stabilized at high temperature by a corresponding positive entropy term, which in large measure must arise from cation disorder.

This work on the spinels drew our attention to the general problems associated with the thermochemistry of cation disorder in mixed oxides at high temperatures. The ideal spinel structure consists of a cubic close packed array of anions, with one-eighth of the tetrahedral and one-half of the octahedral interstitial sites occupied by cations. Hence the cation to anion ratio will be 3:4. In a simple oxide spinel, AB_2O_4 , two extreme distributions of cations are possible: the "normal" distribution $\text{A}(\text{B}_2)_2\text{O}_4$, and the "inverse" distribution $\text{B}(\text{AB}_2)_2\text{O}_4$, in each case the ions in parenthesis occupy octahedral sites. Intermediate distributions also are known, which may conveniently be described in terms of an "inversion parameter," x :

$\text{Al}(\text{B}_2)\text{O}_4 \rightleftharpoons \text{A}_x(\text{B}_{2-x}\text{A})_2\text{O}_4$.

For $x=0$, we have the "normal" spinel, for $x=1$, the "inverse" spinel, for $x=2/3$ the "random" spinel.

Navrotsky and Kleppa²² gave a general discussion of the thermodynamics of cation distributions in spinels. I reproduce from their work Fig. 10, which shows the dependence of the configurational entropy on the parameter x . In view of this graph it will readily be understood why some spinels with significant positive enthalpies of formation may well be stable at elevated temperatures.

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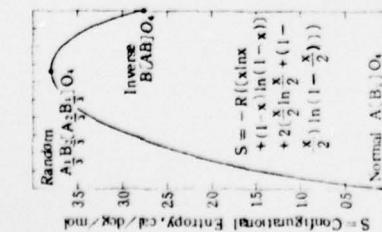


Fig. 10. Configuration entropy in disordered spinels as a function of degree of inversion, x .

sites by α , β , γ , δ , the preferred structural arrangement at low temperatures will be the ordered structure characteristic of "low albite": $(\text{Al})_\alpha (\text{Si})_\beta (\text{Al})_\gamma (\text{Si})_\delta$ with a zero configuration entropy.

However, at sufficiently high temperatures it is found that the Al and Si atoms will assume the random distribution $(\text{Al})_\alpha \text{Si}_\beta (\text{Al})_\gamma \text{Si}_\delta (\text{Al})_\epsilon \text{Si}_\zeta (\text{Al})_\eta \text{Si}_\nu$ with a configuration entropy of $-4R(\ln 0.25 + 0.75 \ln 0.75) = 4.5 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Using oxide melt solution calorimetry, Holm and Kleppa²³ determined the progress of the disordering process in low albite resulting from long term high temperature anneals at 1045°C. The results are shown in Fig. 11. Note that the overall enthalpy difference between the original "low albite" and the fully annealed "high albite" is about 3.4 kcal/mol⁻¹ (at 700°C). Note also that our results indicate that it is possible that the very sluggish disordering process in albite may be a two-step process.

During the past few years we have developed other applications of oxide melt solution calor-

often important thermodynamic differences between the pure, fully ordered samples assumed in most calculations, the rather impure samples provided by nature, and the sometimes disordered materials prepared and used in the high temperature-high pressure laboratory. We may make significant mistakes in our calculations unless these differences are recognized and taken into account.

In many cases we have been able to overcome these difficulties by coordinating high temperature-high pressure equilibrium work with oxide melt solution calorimetry. If calorimetric work is carried out directly on samples of minerals which are consumed or generated in the equilibrium work, the measured enthalpy changes relate to the substances which are actually under investigation. From a comparison between the Gibbs energies calculated from the equilibrium data, and the enthalpies obtained from calorimetry, it will also often be possible to obtain reliable entropy information valid at the temperatures of the equilibrium study. Such information may provide further insight with respect to cation disorder in the system being studied, and on the slope of the P/T curve of interest. This approach has provided a valuable new handle on some important mineral equilibria.²⁷

4. Reaction Calorimetry of Solids

Some of the principal applications of this technique have been:

- (1) Direct Solid-Solid Reactions. This experimental approach was first applied by Kubaschewski and Wulff in a study of the enthalpies of formation of intermetallic compounds such as CaPb_6 . An intimate mixture of the powders of the two metals in the form of a compacted pellet is dropped from room temperature into the calorimeter at 700°C. The heating of the sample initiates the solid-solid reaction, which rapidly proceeds to completion in the calorimeter. The same approach was adopted by Yokokawa and Kleppa²⁸ in a determination of the enthalpy of formation of $\text{Pb}_3(\text{VO}_4)_2$ from solid PbO and V_2O_5 .

In both of these examples there was reason to be concerned about the uniformity of composition of the solid reaction product. Even so, this technique has become increasingly apparent that there are

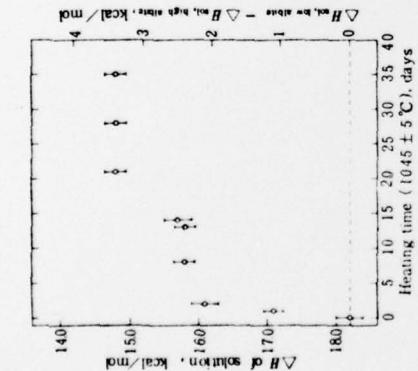


Fig. 11. Enthalpies of solution in lead-cadmium-borate at 700°C of samples of Amelia albite heated for various periods of time at 1045±5°C.

metry in studies of mineral reactions and equilibria.^{26,27} These applications are motivated by the fact that as the number of components and phases in a high temperature-high pressure mineral system becomes greater than 2, the number of possible univariant equilibria may become very large. For example, in the petrologically important ternary system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ there are at least 10 different important solid phases and about 25 univariant mineral equilibria of interest. Obviously, the labor involved in determining all of these equilibria by direct high temperature-high pressure experimentation would be tremendous. In some cases the work also would be impossible because of kinetic considerations which apply in the laboratory, but not necessarily in nature. Hence the great need for relevant thermodynamic and thermochemical data, both for pure minerals and for their solid solutions. The existence of such data would, of course, allow reliable calculations of the equilibrium conditions.

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However, as a result of our recent work on the high temperature thermochemistry of minerals, it has become increasingly apparent that there are

unique should have some real merit in thermochemical studies of fairly exothermic reactions between relatively low melting solids. On the other hand, it will not be suitable for the study of very refractory systems or of silicates.

(2) Phase Transformation Calorimetry. In some cases metastable solid phases (or glasses) can be maintained at room temperature for indefinite periods of time while, by increasing the temperature, transformation to a more stable form can be achieved. These are favorable conditions for high temperature phase transformation calorimetry. We used this technique to determine the enthalpy of transformation of stishovite to silica glass²¹, and of a high pressure polymorph of TiO_2 to the stable rutile modification.²⁹ The method has some things in common with scanning calorimetry, but should be capable of producing more precise thermodynamic information.

(3) High Temperature Combustion Calorimetry. At room temperature combustion calorimetry usually is carried out by means of the oxygen or fluorine bomb calorimeter. This technique remains one of the principal tools of thermochemistry, and may well be superior to all other methods of calorimetry³⁰ when the combustion process gives rise to gaseous and water soluble oxidation products. However, the technique has obvious limitations when the oxidation products are solid substances which fail to reach the fully oxidized form during the calorimetric experiment. In such cases high temperature combustion calorimetry at atmospheric oxygen pressures may be a useful alternative. We have applied this method in thermochemical studies of non-stoichiometric oxides of tungsten³⁰, vanadium³¹, and titanium³².

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(4) Partial Enthalpy Measurements. In 1963, Gerdean, Marucco, and Dode³³ first demonstrated the possibility of direct determinations at high temperatures of the partial enthalpies of oxygen in nonstoichiometric oxides. Since that time Gerdean and coworkers have demonstrated the very considerable potential of this method in calorimetric studies of a number of metal-oxygen systems at temperatures up to about 1500°C.

Our own work in this area has been limited to

metal-hydrogen systems¹⁴⁾, and has been carried out at much lower temperatures than the work of Gerdehan et al. Even so, due to the relatively high experimental precision, our partial enthalpy measurements in metal-hydrogen systems are now contributing significantly to the understanding of the thermodynamics of these very important alloy systems.

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